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PREPARATION AND COMPARISON OF THE PHOTOELECTRONIC PROPERTIES OF--ETC(U)

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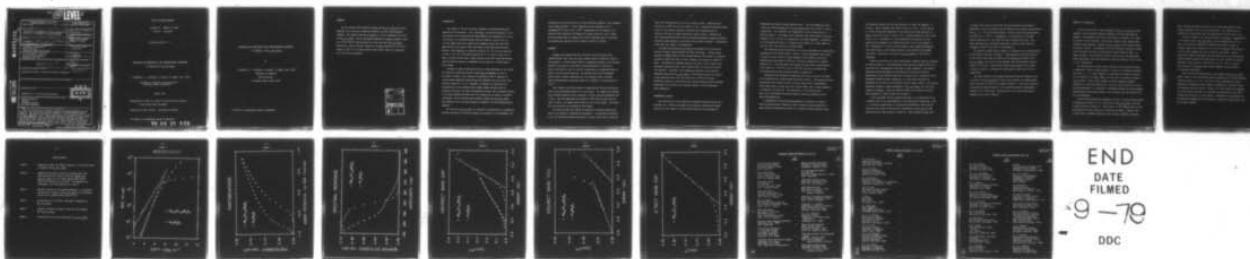
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 6	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Preparation and Comparison of the Photoelectronic Properties of $\text{Sr}_{2}\text{Nb}_{2}\text{O}_{7}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_{2}\text{O}_{6}$		5. TYPE OF REPORT & PERIOD COVERED ⑦ Technical rept.
6. AUTHOR(s) Aaron/Wold, J./Hormadaly, S. N./Subbarao, R./Kershaw K./Dwight		6. PERFORMING ORG. REPORT NUMBER 15 6
7. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Brown University Providence, Rhode Island 02912		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0387
9. CONTROLLING OFFICE NAME AND ADDRESS Dr. David Nelson, Code 472 Office of Naval Research Arlington, Virginia		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-359-653
11. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) ⑪ 24 Aug 79		12. REPORT DATE 8/20/79
		13. NUMBER OF PAGES 23
		15. SECURITY CLASS. (of this report) ⑫ 24p.
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; Distribution unlimited ⑭ TR-6		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted to J. of Solid State Chemistry		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photoelectrolysis Bandgap Flat-band potential Structure Dependence		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The two alkaline earth niobates $\text{Sr}_{2}\text{Nb}_{2}\text{O}_{7}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_{2}\text{O}_{6}$ have been prepared, their electronic properties measured, and their photoresponses compared. The indirect band gap in $\text{Sr}_{2}\text{Nb}_{2}\text{O}_{7}$ is 3.86 eV compared with 3.38 eV for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_{2}\text{O}_{6}$ . Hence, photoanodes composed of $\text{Sr}_{2}\text{Nb}_{2}\text{O}_{7}$ respond to much less of the white light spectrum than those made from $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_{2}\text{O}_{6}$ . Nevertheless, their electrical outputs at an anode potential of 0.8 eV with respect to SCE in 0.2 M sodium acetate under "white" xenon arc irradiation of 1.25 W/cm <sup>2</sup> are comparable.		

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Contract No. N00014-77-C-0387

Task No. NR-359-653

Technical Report No. 6

PREPARATION AND COMPARISON OF THE PHOTOELECTRONIC PROPERTIES

of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$

J. Hormadaly, S. N. Subbarao, R. Kershaw, K. Dwight, and A. Wold<sup>\*</sup>

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August, 1979

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PREPARATION AND COMPARISON OF THE PHOTOELECTRONIC PROPERTIES

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by

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## ABSTRACT

The two alkaline earth niobates  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  have been prepared, their electronic properties measured, and their photoresponses compared. The indirect band gap in  $\text{Sr}_2\text{Nb}_2\text{O}_7$  is 3.86 eV compared with 3.38 eV for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ . Hence, photoanodes composed of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  respond to much less of the "white" light spectrum than those made from  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ . Nevertheless, their electrical outputs at an anode potential of 0.8 eV with respect to SCE in 0.2 M sodium acetate under "white" xenon arc irradiation of  $1.25 \text{ W/cm}^2$  are comparable.

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## INTRODUCTION

Few reports of the use of niobium compounds for photoelectrodes have appeared in the literature. For n-type  $\text{Nb}_2\text{O}_5$ , an optical band gap of 3.4 eV was observed, and the measured flat-band potential was reported to be -1.0 eV with respect to a saturated calomel electrode (SCE) at a pH of 13.3 (1). It would appear that other niobium oxide compounds should also have band gaps which are too large to make them useful as photoelectrode materials. However, n-type  $\text{Hg}_2\text{Nb}_2\text{O}_7$  was reported by Kung et al. (2) to have a band gap of only 1.8 eV, but a flat-band potential of 0.1 V vs SCE at a pH of 13.3. Hence, the gain of utilizing a larger portion of the solar spectrum obtained from the smaller band gap is compensated by the need for a larger applied bias voltage.

Although it might be anticipated that the large difference in the optical and electronic properties between n-type  $\text{Nb}_2\text{O}_5$  and  $\text{Hg}_2\text{Nb}_2\text{O}_7$  are due to the effect of Hg(II), there remains the possibility that a comparison of niobium-oxygen compounds crystallizing with different structures would show different properties. It is, therefore, of interest to investigate the photoresponses of two alkaline earth niobium oxides crystallizing with different structures, but where the photoactive center can be assigned uniquely to the  $\text{NbO}_6$  octahedra and where the A-ions chosen are as similar as possible. Accordingly, the two alkaline earth niobates  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  were prepared, their electronic properties measured, and their photoresponses compared.

The compound  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  was reported to crystallize as a tetragonally distorted perovskite, (3) whereas  $\text{Sr}_2\text{Nb}_2\text{O}_7$  was reported to be orthorhombic (4).



Although the two structures have not been determined completely, both compounds contain  $\text{NbO}_6$  octahedra. If both compounds could be prepared so as to accommodate  $\text{Nb}^{4+}$  ions as well as  $\text{Nb}^{5+}$ , compensating for the change in the valence of the niobium by the formation of oxygen vacancies, then it might also be possible that the conductivity of both compounds could be controlled by adjusting the condition for the reduction of  $\text{Nb(V)}$  to  $\text{Nb(IV)}$ .

#### SYNTHESIS

$\text{Sr}_2\text{Nb}_2\text{O}_7$  was prepared from the solid-state reaction between  $\text{SrCO}_3$  (Johnson Mathey, spec. pure) and  $\text{Nb}_2\text{O}_5$  (Kawecki Beryco Industries, spectroscopic grade). A finely ground mixture of appropriate amounts of the starting materials was placed in a platinum crucible and heated at  $1150^\circ\text{C}$  for a total of 120 hours in order to obtain a single phase, as determined from its powder x-ray diffraction spectrum. The heating process was interrupted several times to permit regrinding and x-ray analysis using a Phillips Norelco Diffractometer using  $\text{CuK}\alpha$  radiation ( $1.5405\text{\AA}$ ) at a scan rate of  $0.5^\circ 2\theta \text{ min}^{-1}$ .

Disks formed by pressing aliquots of approximately 130 mg at 60,000 psi were placed on platinum supports in a cold furnace. The temperature settings were increased stepwise at hour intervals to  $1115^\circ\text{C}$ , which was maintained for 5 hours. Then the temperature was raised to  $1330^\circ\text{C}$  and was held there for about 15 hours. The samples were allowed to cool in the furnace. Pure white, well sintered disks were obtained by this method.

The sintered disks were reduced by heating in evacuated sealed silica tubes in the presence of powdered Nb (Atomergic). As described by Schleich, et al, (6) the niobium powder was placed in a small silica tube, so that the

sample and reducing material were not in direct contact. Reductions were carried out at 900°C for various lengths of time. Although the measured resistivities of the products continued to decrease with increasing time of reduction, the rate of change became small after 67 hours. Reduction for this time produced blue-white disks which showed negligible change in measured resistivity upon abrasion to two-thirds their original thickness. Consequently, these disks were judged to be homogeneous.

The defect perovskite  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  was prepared by the solid-state reaction of  $\text{BaCo}_3$  (Johnson Mathey) and  $\text{SrCo}_3$  with  $\text{Nb}_2\text{O}_5$ . A finely ground mixture of weighed amounts of the starting materials was heated in a platinum crucible at 1100°C for about 42 hours, reground, and heated for another 40 hours. The product was reground, pressed into disks of about 130 mg, and sintered as described above. Well sintered disks of a faint yellow color were obtained. The powder x-ray diffraction spectrum of this material indicated single-phase  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ . The reduction process was similar to that described above, but was carried out at 750°C for 60 hours. Essentially identical resistivities were measured before and after abrading these disks to two-thirds their original thickness, which established their homogeneity.

#### EXPERIMENTAL RESULTS

The resistivities of the samples were measured using the Van der Pauw technique (6). Contacts were made by the ultrasonic soldering of indium directly onto the samples, and their ohmic behavior was established by



measuring their current-voltage characteristics. The room temperature resistivities of reduced  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  disks were 35 and 1.6 ohm-cm, respectively. The variations with temperature of these resistivities are shown in Figure 1. The slopes of the indicated lines yield thermal activation energies of 0.12 and 0.18 eV, respectively, for these compounds. In addition, the low temperature behavior of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  shows evidence of a small number of carriers with a much smaller activation energy.

The reduced materials were proven to be n-type semiconductors by qualitative measurement of the Seebeck effect. However, routine measurements were unable to detect any Hall voltage in these compounds, which indicates that their mobilities are less than  $0.1 \text{ cm}^2/\text{V-sec}$ , as would be expected for a hopping conductor (7). Given the above resistivities, minimum carrier concentrations of the order of  $2 \times 10^{18} \text{ cm}^{-3}$  and  $4 \times 10^{19} \text{ cm}^{-3}$  can then be estimated for the strontium and barium strontium niobates, respectively.

Photoanodes were prepared by evaporating thin films of gold on the backs of the reduced disks to provide good electrical contacts. The photoelectrolysis measurements were carried out with a 150 watt xenon lamp, a monochromator (Oriel Model 7240), a glass cell with a quartz window, and a current amplifier as previously described (8). The electrolyte, 0.2 M sodium acetate ( $\text{pH} \approx 8.3$ ), was purged of dissolved oxygen by continuous bubbling of 85% Argon-15% Hydrogen gas.

A comparison of the observed photoresponses is presented in Figure 2, where the photocurrents obtained in "white" light are plotted against the anode potential measured with respect to a saturated calomel electrode (SCE).

The difference between the flat-band potentials of these two compounds is striking. That of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  lies lower by about 0.4 volts. In this context, it is worth noting that adjustment of the reported flat-band potential of  $\text{Nb}_2\text{O}_5$  to a pH of 8.3 gives a value of -0.7 V, midway between the curves shown in Fig. 2 (1). Furthermore, in these experiments the condition of zero applied bias corresponds to an anode potential of -0.63 V with respect to SCE. Consequently, it can be seen from Figure 2 that  $\text{Sr}_2\text{Nb}_2\text{O}_7$  photoanodes yield nearly half as much current unbiased as when biased to the maximum value shown. Conversely, the output of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  at zero bias is negligible.

These two structures also yield significantly different spectral responses, as shown in Figure 3. Both measurements were made with an applied bias of 1.2 volts and with a monochrometer half-width of eight nanometers. The quantum efficiency (electrons/photon) was determined by dividing the observed photocurrent by the incident light flux as measured with a calibrated silicon photodiode (United Detector Technology), no corrections being made for absorption in the cell or for reflection from the sample surface. This quantum efficiency extends to longer wavelengths in  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ , but rises more abruptly in  $\text{Sr}_2\text{Nb}_2\text{O}_7$ . These two effects balance out to produce the nearly equal responses to "white" light seen in Figure 2.

It has been shown that the quantum efficiency  $\eta$  of a photoanode can be a powerful tool for the determination of interband optical transitions, since  $\eta$  is directly proportional to the absorption coefficient  $\alpha$  when both the depletion layer width ( $W$ ) and the hole recombination length ( $L_p$ ) are much smaller than the light penetration depth (9). These conditions imply that

$\eta$  be small, which can be verified for both these materials from Figure 3. Furthermore, it can be estimated from the mobilities and carrier concentrations that  $L_p < W < 10^{-6}$  cm for both niobates, so that the desired proportionality will hold for  $\alpha \leq 10^6$  cm<sup>-1</sup>. Consequently,  $\eta(h\nu - E_g)^2/h\nu$  for an allowed indirect band gap, and  $\eta(h\nu - E_g)^{0.5}/h\nu$  for an allowed direct gap. Thus these band gaps can be obtained, respectively, from the linear portions of graphs of  $(\eta h\nu)^{0.5}$  and  $(\eta h\nu)^2$  vs the energy  $h\nu$ .

The spectral response data of Figure 3 is replotted for the determination of the indirect band gaps in Figure 4. Extrapolation of the linear portion of the curves yield values of 3.86(2) eV for  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and 3.38(2) eV for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ , the latter in fair agreement with the previously reported value of 3.28 eV (9). Both of these indirect gaps possess "tails" which, as shown in Figure 5, correspond to energy gaps of 3.36(4) and 2.6(1) eV, respectively.

The rapid increase in the quantum efficiency below 280 nanometers seen in Figure 2 for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  is due to the existence of a higher-energy direct band gap at 4.44(2) eV, as shown in Figure 6. This result supercedes the previously reported value of 4.2 eV, which was based on measurements limited to 4.6 eV and below. No evidence for such a direct band gap for  $\text{Sr}_2\text{Nb}_2\text{O}_7$  can be seen in Figure 3.



## SUMMARY AND CONCLUSIONS

The two alkaline earth niobates  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  have been prepared, their electronic properties measured, and their photoresponses compared. The compounds crystallize with different structures, but contain as similar A-ions as possible. Both niobates become n-type, hopping semiconductors upon reduction. However,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  is more easily reduced by metallic niobium, as evidenced by the lower reduction temperature needed and by the lower resistivity attained after similar reduction times. As shown in Figure 1, the variations of their resistivities with temperature differ appreciably, with room temperature activation energies of 0.13 eV and 0.18 eV, respectively.

The photoresponses of both niobates studied can be attributed uniquely to photoactive centers of  $\text{NbO}_6$  octahedra, as can also the properties reported for  $\text{Nb}_2\text{O}_5$  (1). In a similar fashion, the photoelectric properties reported in the literature for  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ , and  $\text{TiO}_2$  can be attributed uniquely to  $\text{TiO}_6$  octahedra. Both of these systems of related compounds encompass differences in structure and/or A-ion. Hence, by cross-correlation of their observed properties, it is possible to distinguish between those photoresponse characteristics which depend primarily upon structure and those dominated by A-ion contributions.

From the photoresponse data presented in Figure 2, the flat-band potential of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  was found to lie 0.4 V below that of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ , with that of  $\text{Nb}_2\text{O}_5$  falling in between (1). This result is to be compared with the flat-band potential of  $\text{SrTiO}_3$  being 0.6 V below that of  $\text{BaTiO}_3$ . However, both of these latter compounds crystallize with the same, perovskite structure.

Thus, one may conclude that variations in the flat-band potential among related compounds is due to A-ion contributions. The substitution of strontium for barium lowers the flat-band potential by about half a volt.

As seen in Figure 4, the indirect band gap in  $\text{Sr}_2\text{Nb}_2\text{O}_7$  is approximately 0.5 eV greater than in  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  (3.86 eV compared with 3.38 eV), with an even greater difference in the band tails shown in Figure 5. A higher energy direct band gap of 4.44 eV can be determined from Figure 6, for the latter compound, but none is found for the former. However, essentially identical band gaps have been reported for the two perovskites  $\text{SrTiO}_3$  and  $\text{BaTiO}_3$  despite the substitution of A-ions, whereas the optical band gap in  $\text{TiO}_2$  (rutile) is smaller by 0.4 eV (2). Thus, it appears that variations in band gap among related compounds are due primarily to structural differences.

Given the values determined above, both  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  adhere closely to the relationship between energy gap and flat-band potential observed by Kung, et al. (2). The span in values represented by these compounds with photoactive  $\text{NbO}_6$  centers is comparable to the span reported for compounds with  $\text{TiO}_6$  centers. However, the values reported for  $\text{Hg}_2\text{Nb}_2\text{O}_7$  lie so far outside this span as to preclude any possibility of the shift arising from structural or A-ion effects. Consequently, the properties of the pyrochlore  $\text{Hg}_2\text{Nb}_2\text{O}_7$  must be attributed to photoactive  $\text{HgO}_8$  centers, and not to  $\text{NbO}_6$  octahedra.



Because of its larger band gap, photoanodes composed of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  respond to much less of the "white" light spectrum than those made from  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ . Nevertheless, their electrical outputs at an anode potential of 0.8 V vs SCE are comparable, as shown in Figure 2. This circumstance arises because of the rapid increase in the quantum efficiency of the former compound at wavelengths just below the band edge, as seen in Figure 3. Thus, the value of the optical band gap does not by itself determine the spectral response of a photoanode; the slope of the quantum-efficiency versus photon-energy curve is also important. The results of this investigation suggest that this important parameter may be structure dependent. Further study of such a structural dependence would be desirable.

#### ACKNOWLEDGEMENTS

The Office of Naval Research, Arlington, Virginia supported the work of S. N. Subbarao and K. Dwight. Acknowledgement is made to the Solar Energy Research Institute, Golden, Colorado for the support of J. Hormadaly. In addition, the authors would like to acknowledge the support of the Materials Research Laboratory Program at Brown University. The authors also wish to express their thanks to Dr. Lothar Brixner of E. I. DuPont de Nemours & Company, Wilmington, Delaware for several helpful discussions.

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FIGURE CAPTIONS

- Figure 1 - Comparison between the thermal variations of the resistivities of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ .
- Figure 2 - Comparison between the variations of photocurrent with anode potential with respect to SCE for  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  in 0.2 M sodium acetate under "white" xenon arc irradiation of  $1.25 \text{ W/cm}^2$ . Zero applied bias corresponds to an anode potential of -0.63 V.
- Figure 3 - Spectral variation of the quantum efficiency  $\eta$  in electrons per photon for  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$  in 0.2 M sodium acetate with an applied anodic bias of 1.2 V.
- Figure 4 - Determination of the indirect band gaps in  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ .
- Figure 5 - Comparison between the indirect band tails for  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ .
- Figure 6 - Determination of the direct band gap in  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ .



FIGURE 1

# RESISTIVITY

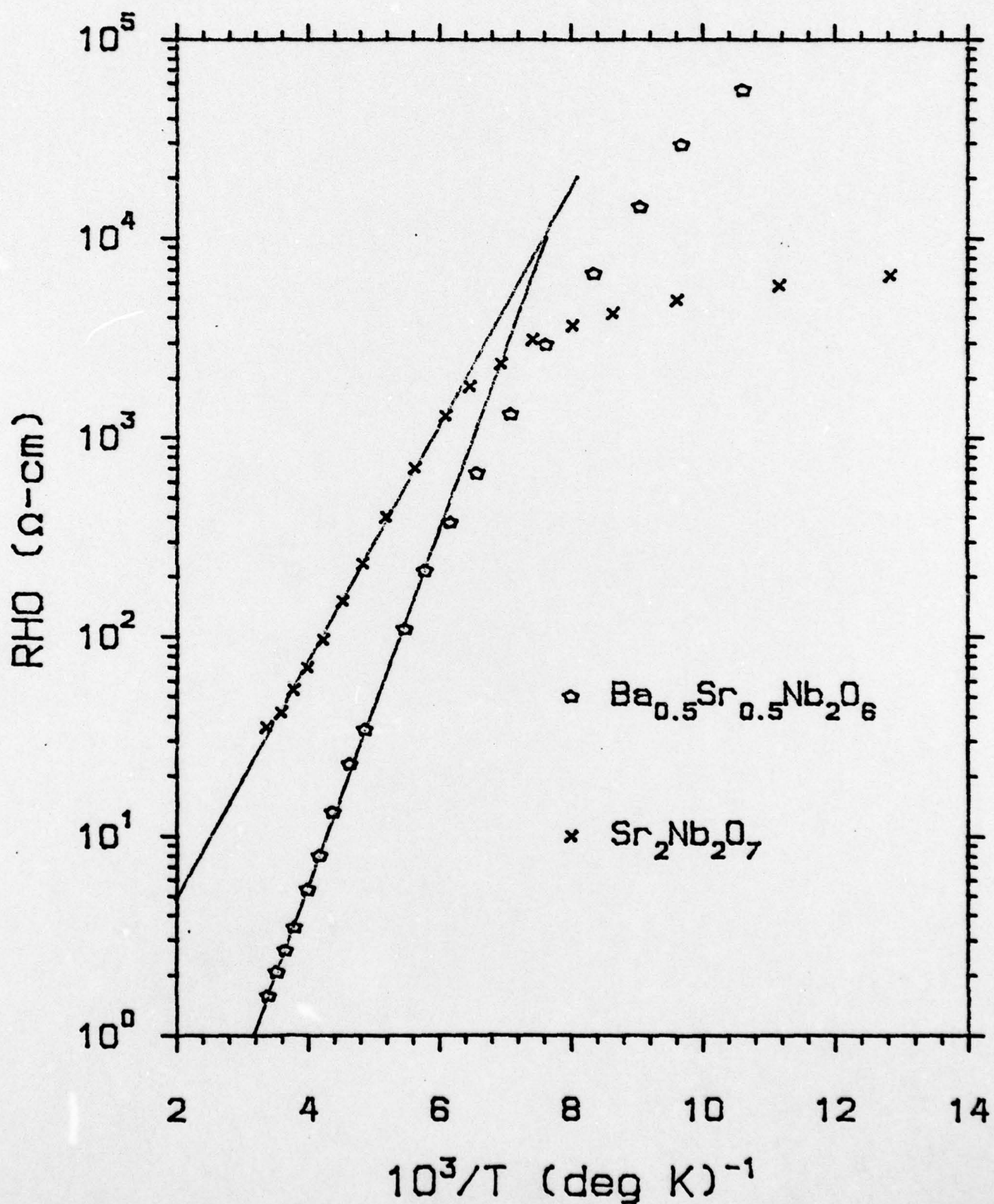


FIGURE 2

PHOTORESPONSE

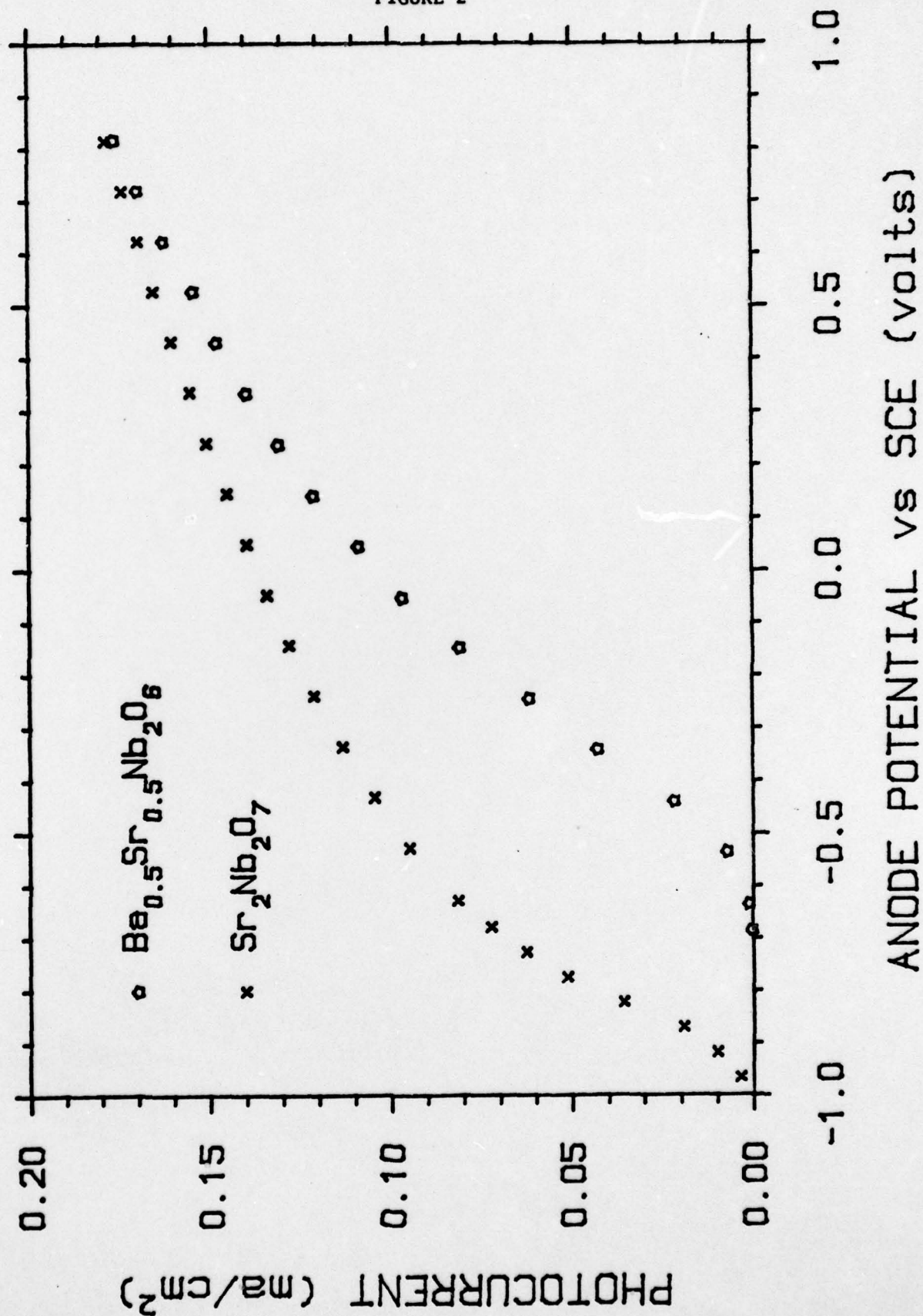




FIGURE 3

# SPECTRAL RESPONSE

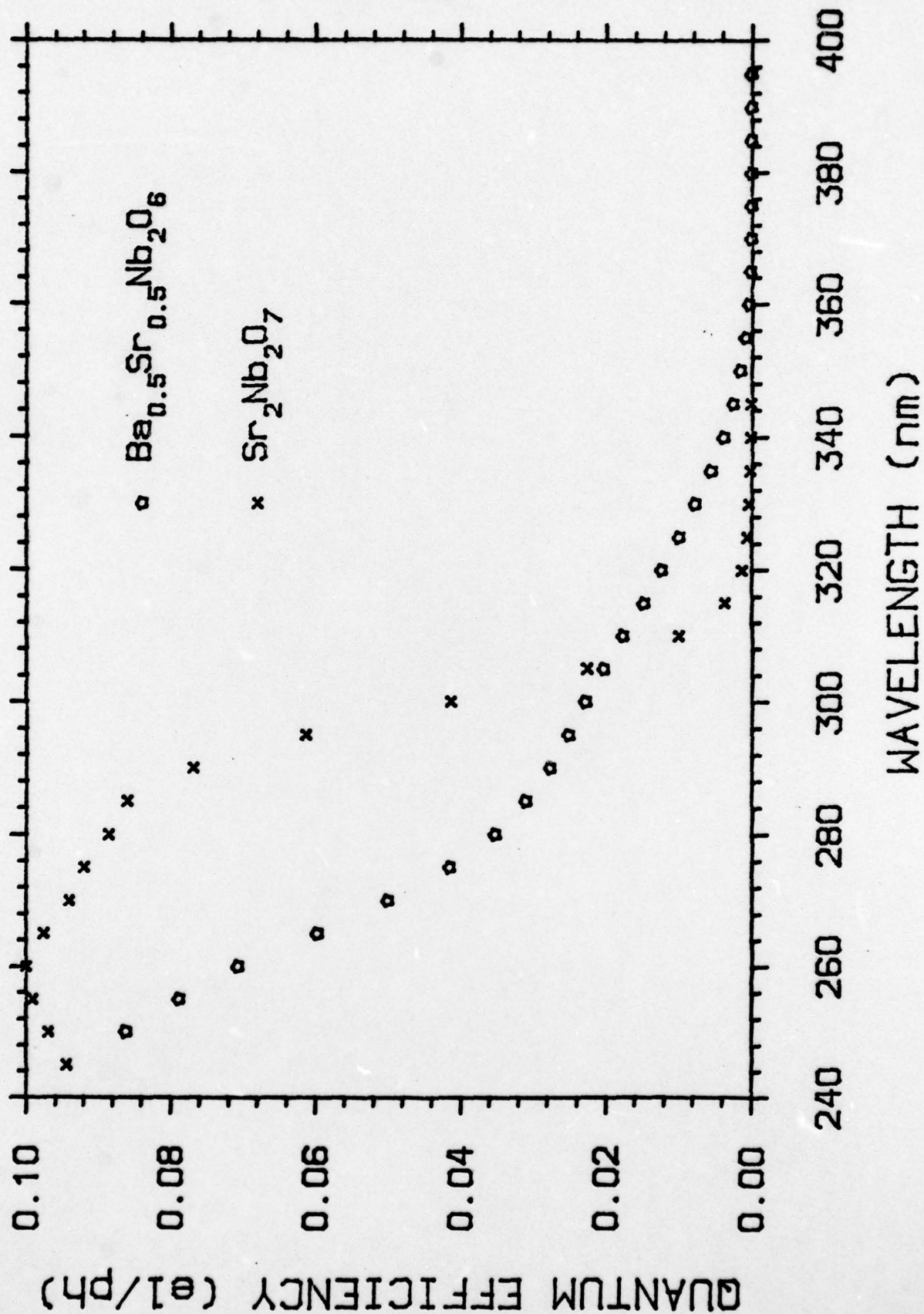


FIGURE 4

# INDIRECT BAND GAP

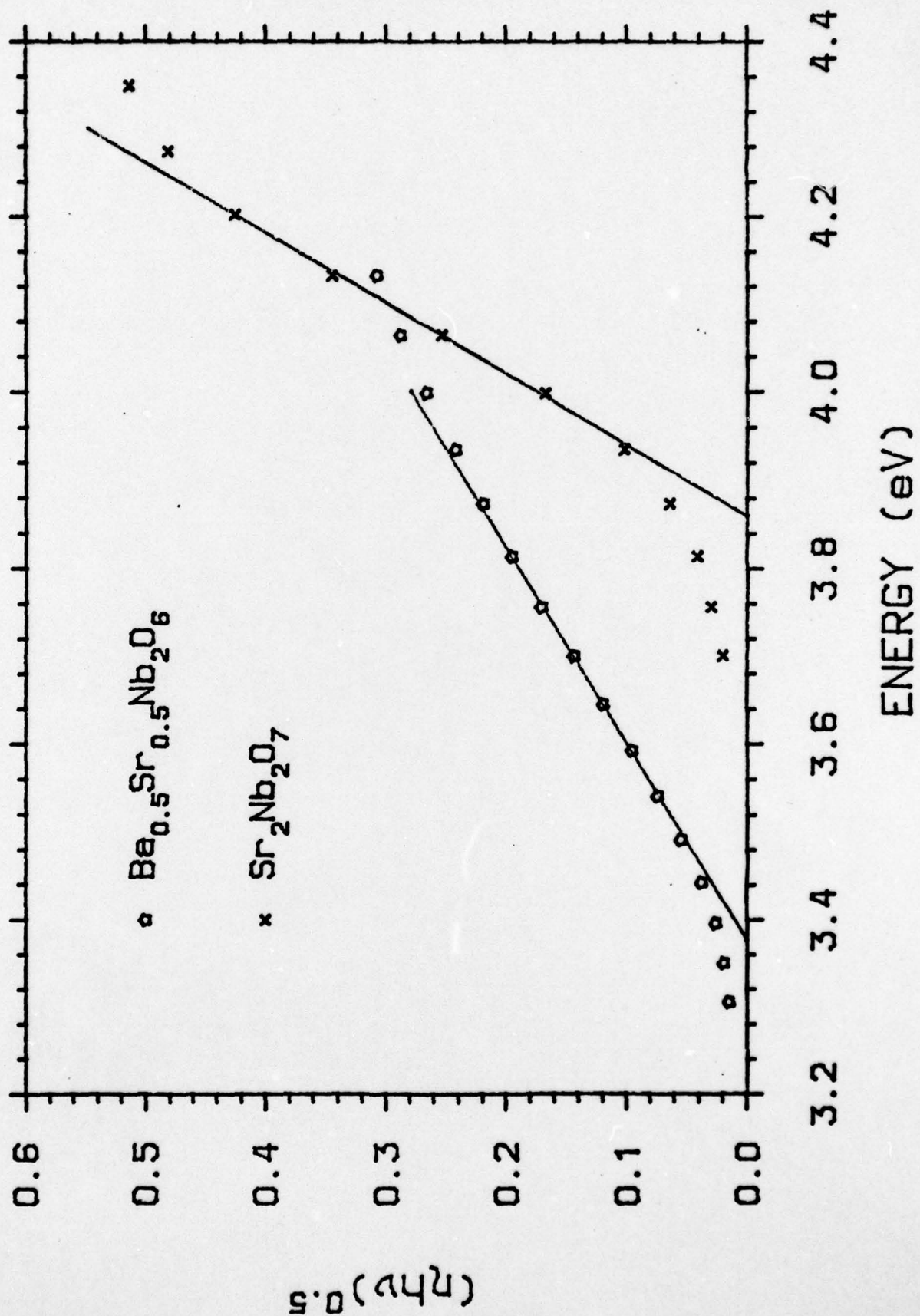


FIGURE 5

# INDIRECT BAND TAIL

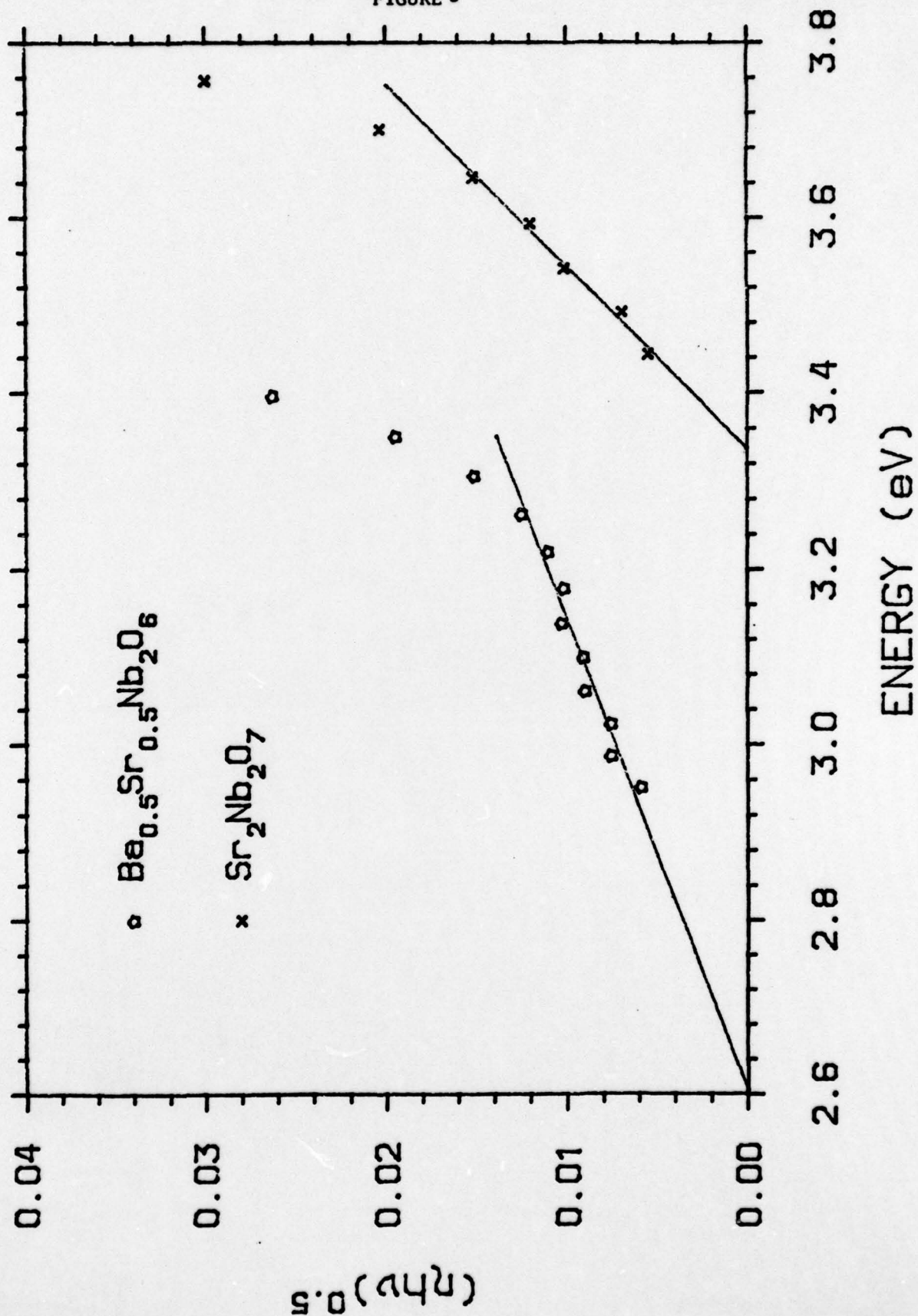
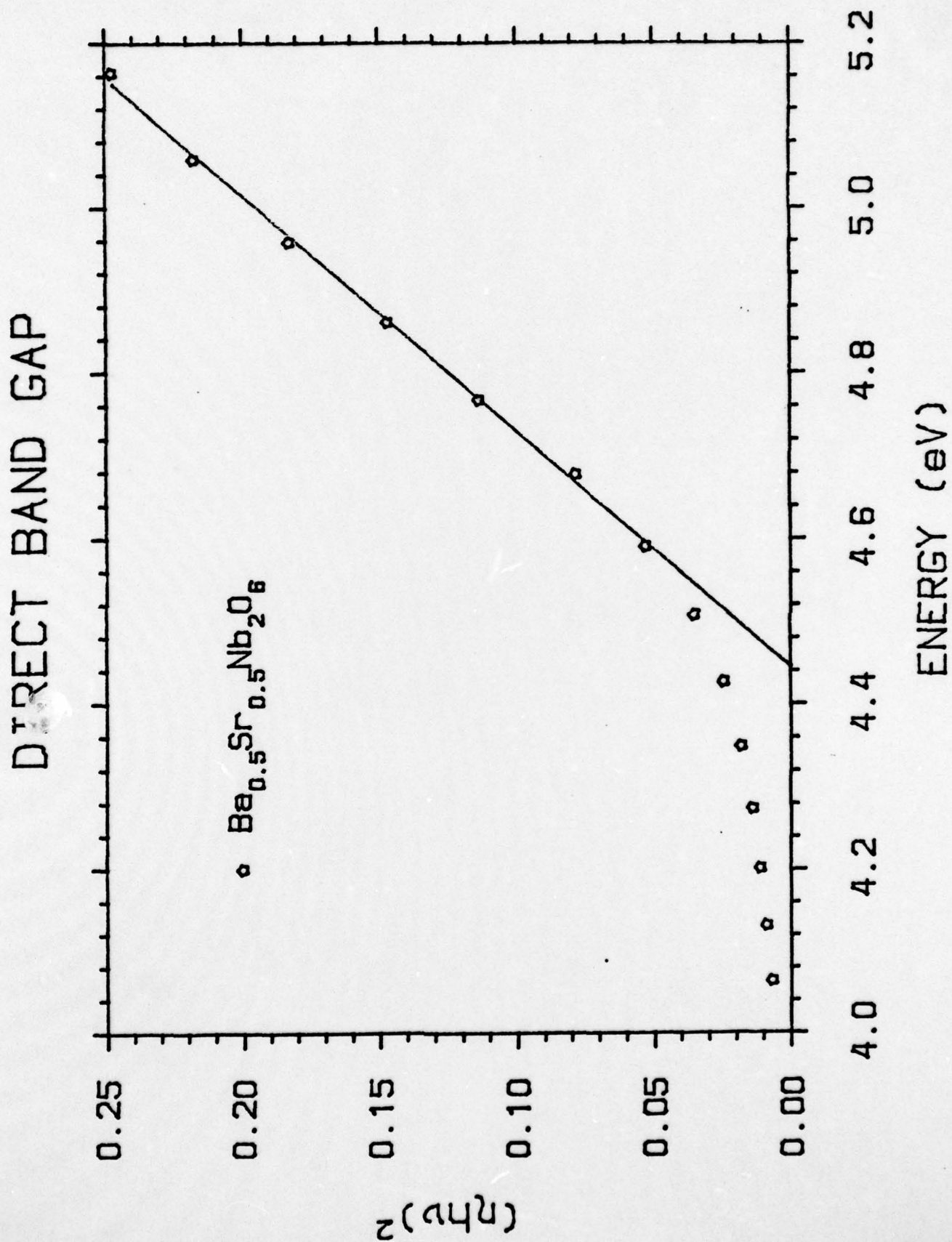




FIGURE 6



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